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## **Polyfire project- an example of an industrial research project promoting safe industrial production of fire-resistant nanocomposites**

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**Abstract.** New developments based on nanotechnology have to guarantee safe products and processes to be accepted by society. The Polyfire project will develop and scale-up techniques for processing halogen-free, fire-retardant nanocomposite materials and coatings based on unsaturated polyester resins and organoclays. The project includes a work package that will assess the Health and Environmental impacts derived from the manipulation of nanoparticles. This work package includes the following tasks: (1) Identification of Health and Environment Impacts derived from the processes, (2) Experimentation to study specific Nanoparticle Emissions, (3) Development of a Risk Management Methodology for the process, and (4) A Comparison of the Health and Environmental Impact of New and Existing Materials. To date, potential exposure scenarios to nanomaterials have been identified through the development of a Preliminary Hazard Analysis (PHA) of the new production processes. In the next step, these scenarios will be studied and simulated to evaluate potential emissions of nanomaterials. Polyfire is a collaborative European project, funded by the European Commission 7<sup>th</sup> Framework Programme (Grant Agreement N° 229220). It features 11 partners from 5 countries (5 SMEs, 3 research institutes, 2 large companies, 1 association) and runs for three years (1st September 2009 – 31st August 2012). This project is an example of an industrial research development which aims to introduce to the market new products promoting the safe use of nanomaterials.

### **1. Introduction**

The number of consumer goods based on nanotechnology is expected to significantly increase in future years, and with it, the number of industrial settings that incorporate nanomaterials in their production process. To date, there is a knowledge gap and also concern related to the potential health and environment impact of nanomaterials. To be accepted by society, nanotechnology based products and processes have to ensure their safety.

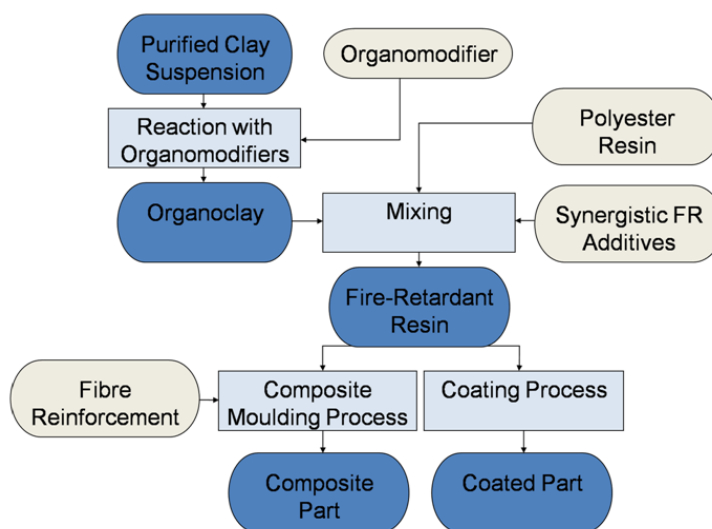
As toxicology science doesn't yet have conclusive results related to the potential harmful effects of nanomaterials, the current approach for occupational risk management is to characterize the exposure

to nanomaterials in order to propose measures to control risks as much as possible. ENRHES project [1] showed that there are very few studies of occupational exposure assessment, with those that do exist mainly focused on carbon based nanomaterials (fullerenes and carbon nanotubes) and performed principally in lab settings. The ongoing NANEX project [2] also seems to corroborate that result, jointly with the difficulties to develop Exposure Scenarios with the actual information, and the need to develop standards for exposure risk characterization, including the measurement strategy and equipment. With regard to exposure to nano-sized clay particles specifically (focus of this work), very few studies have been found by the researches. Schnaider et al [3] addressed the study of the dustiness of powders, including bentonite and organoclays, as a potential tool to simulate personal exposure to nanopowders, while Jankowska et al [4] in the NANOSH project analyzed the emission of nanosized particles in the process of clay blending for the production of new fire-safe foams. On the other hand, related to measures to control exposure, research already done seems to show that control engineers and personal protection equipment could provide different protection levels against nanomaterials [5].

The aim of the Polyfire project is to develop and scale-up techniques for processing halogen-free, fire retardant (FR) nanocomposite materials and coatings based on unsaturated polyester resins and clays. In this project a Health and Environment (H&E) assessment of the new processes and products will be performed, focused on the study of potential exposure to nano-sized organoclay particles in order to finally propose a risk management methodology. To date a Preliminary Hazard Assessment (PHA) has been performed, where potential exposure scenarios to organoclays have been identified. In this paper we present this project, as an example of an industrial research development which aims to introduce to the market new products promoting the safe use of nanomaterials.

## 2. Polyfire project

The Polyfire project is structured in 8 work packages devoted to research on industrial processes for the production of new fire retardant nanocomposites and coatings based on unsaturated polyester resins and clays. A dedicated work package is focused on assessment of the main health and environmental impacts derived from these new processes. Figure 1 gives an example of the industrial process for fire retardant nanocomposite and coating production.



**Figure 1.** General processes to develop new fire retardant nanocomposites/coatings.

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It is important to mention that to date there is no clear evidence for the presence of nanoparticles in the unsaturated polyester composites produced in this project. The x-ray diffraction evidence suggests that an intercalated nanocomposite or a microcomposite is being produced. Nevertheless, the position being taken is that there is the potential to generate nanoparticles during organoclay production, the mixing of organoclay with the resin and during handling of the molded component (for example when it is cut or sanded). Therefore, the Health and Environmental (H&E) assessment is designed to evaluate the type and nature of any nanoparticles generated, identify adequate control measures and educate relevant individuals and companies of adequate control measures.

### **3. The approach for the Health and Environment Assessment**

Within the H&E assessment, 4 tasks will be performed: (1) Identification of Health and Environment (H&E) Impacts derived from the processes, (2) Experimentation to study specific Nanoparticle Emissions, (3) Development of a Risk Management Methodology for the process, and (4) A Comparison of the Health and Environmental Impact of New and Existing Materials. In the first year of Polyfire, task 1 has been performed.

The approach followed in task 1 (identification of H&E impacts) has been to identify potential workers exposure to organoclay particles jointly with environmental emissions. To perform it two tools have been used, a Preliminary Hazard Analysis (PHA) and an Impact Matrix (IM).

The PHA started with the analysis of the processes covering the life cycle of the new fire retardants. In the scope of this project, we have considered the production process, the professional use and the end of life of the new FR products with a main focus on the production stage. The analysis of the different industrial tasks and activities has been performed in collaboration with the partners involved in each stage of the cycle. Normal operation, emergency conditions (e.g. breakages, releases) and other tasks, such as cleaning/maintenance procedures have all been considered. The information collected in this process has been introduced in templates for each step of the processes with the key relevant information. Afterwards, for each of the steps analyzed in the previous activity, the hazards related to the potential exposure to organoclay particles have been identified. The analysis of workers hazards has focused on inhalation, although dermal exposure has been also identified. Hazard of inhalation has been ranked as High-Medium-Low based on the presentation of the organoclay particle (powder/suspension/embedded in matrix), type of system (open/closed) and the operation performed (subjected to high energy). Regarding environmental hazards, in the PHA the environmental aspects with potential significance have been identified [6]. Both, the occupational and environment PHA has been collected in templates designed for it.

Finally, the results of the PHA has been summarized in an Impact Matrix (IM) which summarizes the steps of the analyzed processes involved in the life cycle of the new FR, and the identified occupational and environmental hazards (see figure 2).

|            |         |                                    |                  | Hazards                          |        |                     |             |       |
|------------|---------|------------------------------------|------------------|----------------------------------|--------|---------------------|-------------|-------|
|            |         |                                    |                  | Occupational                     |        | Environment         |             |       |
|            |         |                                    |                  | Inhalation                       | Dermal | Atmospheric release | Waste Water | Waste |
| PRODUCTION | PROC X: | Step A<br>Organoclay milling       | N <sup>(1)</sup> | Organoclay transfer              | Low    |                     |             |       |
|            |         |                                    |                  | Grinding process                 | Low    | X                   |             |       |
|            |         |                                    |                  | Hatch opening                    | High   | X                   |             |       |
|            |         |                                    | E <sup>(2)</sup> | Spilled organoclay               | High   | X                   | X           | X     |
|            |         |                                    | O <sup>(3)</sup> | Maintenance/cleaning             | High   | X                   | X           | X     |
|            |         | .....                              | .....            | .....                            | .....  | .....               | .....       | ..... |
|            |         | Step B<br>Organoclay+ resin mixing | N                | Organoclay feeding               | Low    |                     |             |       |
|            |         |                                    |                  | Powder liquid high shear mixing  | Low    |                     |             |       |
|            |         |                                    |                  | Hatch opening- sample collection | Med    | X                   |             |       |
|            |         |                                    | E                | Spilled organoclay               | High   | X                   |             | X     |
|            |         |                                    | O                | Maintenance/cleaning             | Med    | X                   |             | X     |
|            |         | .....                              | .....            | .....                            | .....  | .....               | .....       | ..... |
|            |         | Step C<br>Composite Machinig       | N                | Handling of composite            | Low    | X                   |             |       |
|            |         |                                    |                  | Composite machining              | Med    | X                   |             |       |
|            |         |                                    | E                | Breackage                        | Low    | X                   |             | X     |
|            |         |                                    | O                | Maintenance/cleaning             | Low    | X                   |             | X     |
|            |         | .....                              | N                | .....                            | Low    | X                   |             |       |
|            |         | .....                              | E                | .....                            | Low    |                     |             |       |
|            |         | .....                              | E                | .....                            | High   | X                   | X           | X     |
|            |         | .....                              | O                | .....                            | High   | X                   | X           | X     |

(1) Normal operation; (2) Emergency; (3) Other operations (cleaning/maintenance)

**Figure 2.** Example of the Impact Matrix (IM) that summaries the results of the PHA

Figure 3 summarizes the targets/life cycle stages under the scope of this work and the *highest hazards* identified in the study. This figure shows that the highest occupational hazards (in red) are related to activities performed in the production stage of the FR composites/coatings, in tasks with potential dust emission (from organoclay powder). Medium hazard (in orange) is presented in the three stages (production/use/end of life) and associated to three different types of tasks: a) tasks with exposure to aerosols from organoclay suspended in volatile liquids with/without agitation, b) spraying of suspensions with organoclays and, c) machining of solid matrix with embedded organoclays.

As mentioned before, note that as yet there is no clear evidence for the presence of nanoparticles in polymeric matrixes filled with organoclays, or in the organoclays powders themselves.

The goal for the next tasks in Polyfire is to perform studies of nanoparticle emissions. From the PHA and the IM, scenarios will be grouped and selected, and experimental designs will be performed in order to get quantitative data related to the emission of nanomaterials. Greatly assist in evaluating the risks derived from the exposure to organoclay particles and finally to develop a strategy for risk management, the main goal of this workpackage in Polyfire.

| TARGET<br>LIFE CYCLE | Worker  | Environment  | Consumer |
|----------------------|---|--|----------|
| <b>Design</b>        | NC  | NC   | NC       |
| <b>Production</b>    | Tasks with potential dust emission (organoclay particles)- Potential worker inhalation  | Identification of environmental aspect with potential significance | NC       |
|                      | Task with exposure to aerosols from nanoparticles suspended in volatile liquids: with/without agitation; spraying                           |  |          |
| <b>Use</b>           | Machining of solid matrix with organoclays embedded- Potential nanoparticles emissions/worker inhalation                                    | Identification of environmental aspect with potential significance | NC       |
| <b>Maintenance</b>   | NC  | NC   | NC       |
| <b>End of life</b>   | Machining of solid matrix (or operations with dust emission) with organoclays embedded- Potential nanoparticles emissions/worker inhalation | Identification of environmental aspect with potential significance | NC       |

**Figure 3.** Summary of the highest hazards identified in the life cycle stages of the new fire retardants products.

#### 4. Conclusions

The Polyfire project aims to introduce to the market new halogen-free fire retardant composites and coatings based on unsaturated polyester resins and organoclay particles. Although there remains a lack of clear evidence to prove nanoparticles are present in either the un-cured polyester resin or the final composite part, the Polyfire project will continue to study their potential health and environmental impact in order to promote safe industrial production. To date, processes involved in the life cycle of the new products have been analysed, identifying potential hazards for workers and the environment. The next challenges in this project are to characterize the potential emissions of nanomaterials in order to finally propose measures for risk management.

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